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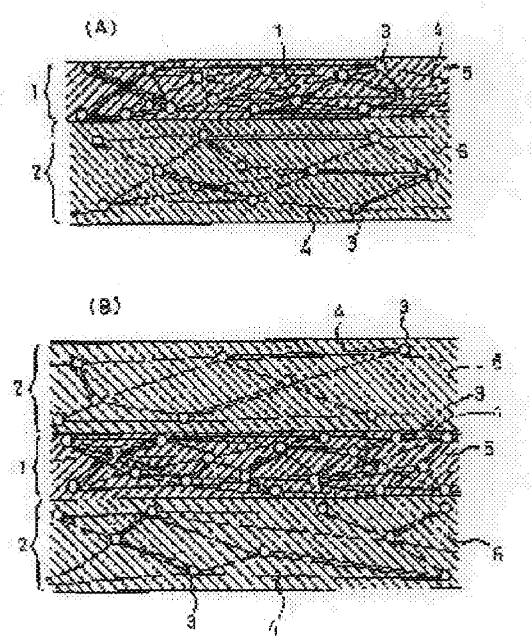
(21)Application number : 07-131771 (71)Applicant : JAPAN GORE TEX INC

(22)Date of filing : 30.05.1995 (72)Inventor : KATO HIROSHI

(54) POLYMER SOLID ELECTROLYTE FILM/ELECTRODE INTEGRALLY MOLDED BODY AND MANUFACTURE THEREOF

(57)Abstract:

PURPOSE: To provide a polymer solid electrolyte/electrode joining body integrally formed with a polymer electrolyte film having uniform thickness, high strength, and the minimum thickness required, and a catalyst layer firmly bonded to the polymer electrolyte film to ensure electrical contact and having high strength.



CONSTITUTION: Stretched porous PTFE is impregnated with a polymer solid electrolyte resin solution 5 then a solvent is removed to form a composite polymer solid electrolyte 1 film, and an electrode 2 formed by filling the electrode 2 constituting component containing at least an electrode catalyst and a polymer solid electrolyte in the pores of the stretched porous PTFE is integrally formed on the surface of the composite polymer solid electrolyte 1 film.

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CLAIMS

[Claim(s)]
[Claim 1]On the surface of a compound polymers solid-electrolyte membrane which consists of extension porosity polytetrafluoroethylene and solid polymer electrolyte resin contained in the porosity hole part. A compound polymers solid-electrolyte membrane / electrode integral-moulding object, wherein an electrode filled up with an electrode configuration ingredient which contains an electrode catalyst and a solid polymer electrolyte at least all over an opening of extension porosity PTFE is formed in one.
[Claim 2]After arranging the 1st extension porosity polytetrafluoroethylene on a substrate which has a mold-release characteristic, by applying a solution of solid polymer electrolyte resin to the surface, Solid polymer electrolyte resin is impregnated all over an opening of extension porosity polytetrafluoroethylene, Remove a solvent, form a compound polymers solid-electrolyte membrane, and the 2nd extension porosity polytetrafluoroethylene membrane is succeedingly arranged on the surface, By applying to the surface an ink-like solution which contains an electrode catalyst and solid polymer electrolyte resin at least, After an ink-like solution is impregnated all over an opening of the 2nd extension porosity polytetrafluoroethylene, A process of the compound polymers solid-electrolyte membrane / electrode integral-moulding object removing a substrate which has a mold-release characteristic and acquiring a compound polymers solid-electrolyte membrane / electrode integral-moulding object after obtaining an electrode by forming it in the polymers solid-electrolyte membrane surface by removing a solvent.
[Claim 3]On the surface of a compound polymers solid-electrolyte membrane which consists of extension porosity polytetrafluoroethylene and solid polymer electrolyte resin contained in the porosity hole part. An electrode filled up with an electrode configuration ingredient which contains an electrode catalyst and a solid polymer electrolyte at least all over an opening of extension porosity PTFE is formed in one, And an electrode / compound polymers solid-

electrolyte membrane / electrode integral-moulding object, wherein an electrode is united also with another surface of this compound polymers solid-electrolyte membrane.

[Claim 4]The electrode / compound polymers solid-electrolyte membrane / the electrode integral-moulding object according to claim 3 in which an electrode filled up with an electrode configuration ingredient which contains an electrode catalyst and a solid polymer electrolyte at least all over an opening of extension porosity PTFE is formed in both sides of said compound polymers solid-electrolyte membrane at one, respectively.

[Claim 5]After arranging the 1st extension porosity polytetrafluoroethylene on an electrode fabricated beforehand, by applying a solution of solid polymer electrolyte resin to the surface, Solid polymer electrolyte resin is impregnated all over an opening of extension porosity polytetrafluoroethylene, Remove a solvent, form a compound polymers solid-electrolyte membrane, and the 2nd extension porosity polytetrafluoroethylene membrane is succeedingly arranged on the surface, By applying to the surface an ink-like solution which contains an electrode catalyst and solid polymer electrolyte resin at least, A process of the electrode / composite high polymer electrolyte film / electrode integral-moulding object forming an electrode in the compound polymers solid-electrolyte membrane surface by removing a solvent after an ink-like solution is impregnated all over an opening of the 2nd extension porosity polytetrafluoroethylene.

[Claim 6]A process of the electrode / composite high polymer electrolyte film / electrode integral-moulding object obtaining by removing a solvent after applying an ink-like solution which contains an electrode catalyst and solid polymer electrolyte resin at least on a substrate which has a mold-release characteristic for said electrode fabricated beforehand in claim 5.

[Claim 7]On a substrate which has a mold-release characteristic for said electrode fabricated beforehand in claim 5, arrange extension porosity polytetrafluoroethylene membrane and an ink-like solution which contains an electrode catalyst and solid polymer electrolyte resin at least on the surface is applied, A process of the electrode / composite high polymer electrolyte film / electrode integral-moulding object obtaining by removing a solvent after an ink-like solution is impregnated all over an opening of extension porosity polytetrafluoroethylene.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to a solid polymer electrolyte/electrode conjugate. Although it can use for the water electrolysis system etc. with which the lithium which uses a lithium ion conductive solid electrolyte in more detail with respect to the electrode / solid polymer electrolyte zygote of the electrochemical device which uses an ion conductivity solid polymer electrolyte used the cell or the proton conductivity solid electrolyte, It is used for the polymers solid oxide fuel cell which uses a proton conductivity solid electrolyte the optimal.
[0002]
[Description of the Prior Art]Much more improvement in energy efficiency is called for, therefore electrode structure is devised, three-dimensions-ize an electrode reaction point, and it is made to increase a labile point, and a solid polymer electrolyte is arranged also inside an electrode, and it enables it to move ion promptly in the electrochemical device which uses a solid polymer electrolyte. In order to be able to move promptly the ion by which it was generated to a counter electrode, contact with the solid electrolyte in an electrode and the solid-electrolyte membrane which is barrier membrane needs to be good, and the membrane resistance of the solid-electrolyte membrane itself needs to be low, and, for that purpose, the thinner possible one of thickness is preferred. If the polymers solid-electrolyte membrane currently used with the fuel cell always is not used by a damp or wet condition, humidify to reactant gas, and are trying to maintain a damp or wet condition indirectly, since polarization occurs and performance falls, an ion-conductive fall and, but. A humidity effect is so good that a polymers solid-electrolyte membrane is thin, and improvement in limiting current density can be expected.
[0003]After preparing a solid-electrolyte membrane and an electrode for according to, respectively and piling these up conventionally, the method of joining with a hotpress is

generally performed.
What was fabricated in the shape of a film as a commercial item as a solid polymer electrolyte (for example, U.S. Du Pont make Nafion #115 grade), the thing which carried out the cast of the solution and fabricated it filmy, etc. are used.
Using it, inserting mechanically, without carrying out a hotpress is also proposed.
[0004]
[Problem(s) to be Solved by the Invention]However, in junction by a hotpress, since a pressure was applied in the place which the film softened with temperature, when thickness was made not much thin, the film was destroyed, and there was a problem of having produced gas leakage or being easy to generate an inter-electrode short circuit. Since this posed a still more difficult problem when the smooth nature of an electrode is bad, it was difficult to make thickness thin extremely. There were also the electrode itself and a problem of spoiling the breathability which is an element whose electrode for enabling the operation with high current density is important since a consolidation is carried out, at the time of a hotpress.
[0005]Although I hear that problems, such as these, are solved and the hot pressing step itself can be skipped and the method of using it, inserting mechanically is also proposed, In order to keep low keeping contact with an electrode uniform, and the contact resistance itself, when a remarkable pressure was needed and thickness was made thin, there was the same problem as a hotpress. In the fuel cell constituted by accumulating two or more cells, it will become what has difficult and low reliability to maintain fixed contact resistance over a long period of time by the stress relaxation of an electrode or a film, etc.
[0006]In order to solve these problems, on an electrode catalyst, the electrode preferably fabricated by the sheet shaped, or an electrode catalyst side, By carrying out spreading desiccation of the solution of solid polymer electrolyte resin, form a solid-electrolyte membrane directly and it is considered as a zygote, . [whether a solid-electrolyte membrane side is made to associate and the hotpress of the zygotes fabricated by carrying out in this way is carried out, and] Or. [whether a solvent is removed after making it associate after applying a solid polymer electrolyte resin solution or its solvent, and unifying, and] Or after making the thing which applied or dried [spreading] the solid polymer electrolyte solution to the inside of sheep dryness too at the electrode or the electrode surface after applying the solution of solid polymer electrolyte resin to an electrode surface associate, removing a solvent and considering it as the anode / film / negative pole integrally molded product is also proposed. However, in the method of applying a solid polymer electrolyte resin solution on an electrode catalyst layer side, and fabricating a film. Depending on electrode structure, film formability may have been bad, and needed to apply the solution too much, therefore osmosis of solid polymer electrolyte resin into an electrode catalyst layer may have become superfluous, and gas diffusion nature may have been checked. It was also difficult to consider it as uniform

thickness, and when it was going to make thickness thin, a possibility of producing an inter-electrode short circuit too was high.

[0007]The high energy efficiency of an electrochemical device in which this invention person used the polymers solid-electrolyte membrane, And it makes it possible to make thickness of a solid-electrolyte membrane thin that the operation with high current density should be made possible, And as the electrode / film zygote, or the electrode / film / electrode conjugate which secures contact resistance with an electrode low and certainly, and does not necessarily need heat pressing distance, without spoiling the original physical properties of an electrode, To an electrode surface, it is extension porosity polytetrafluoroethylene (hereafter). Polytetrafluoroethylene is abbreviated to PTFE. What fabricated to one the compound polymers solid-electrolyte membrane which consists of solid polymer electrolyte resin contained in the porosity cavity part is proposed (the Japanese-Patent-Application-No. No. 303672 [six to] specification). Namely, by applying a solid polymer electrolyte resin solution to the surface, after arranging extension porosity PTFE on an electrode, The cavity part of extension porosity PTFE is impregnated in a solid polymer electrolyte resin solution, and by removing a solvent after that, an electrode and one are used at the same time it forms a compound polymers solid-electrolyte membrane in an electrode surface.

[0008]However, also in this method, when the solid polymer electrolyte solution applied to the surface depending on the physical properties of an electrode penetrates an extension porosity PTFE film and sinks into an electrode, the presentation of an electrode may be changed and it may have an adverse effect on an electrode characteristic. When this phenomenon happens selectively, it is also possible to cause the variation in an electrode characteristic, the thickness of a compound polymers solid-electrolyte membrane, and the variation of resistance.

[0009]Apart from the above thing, this invention person has proposed the catalyst bed which fills up the opening of extension porosity PTFE with the ingredient which includes solid polymer electrolyte resin and a catalyst at least as an electrode for electrochemical devices which used the polymers solid-electrolyte membrane, By constituting this from on a gas diffusion layer material face, what is called a gas diffusion electrode of a gas diffusion layer / catalyst bed one is proposed (the Japanese-Patent-Application-No. No. 304991 [six to] specification). However, in order to be filled up with the ingredient which includes solid polymer electrolyte resin and a catalyst in this electrode in the opening of extension porosity PTFE, it is necessary to use these ingredients as the ink-like solution which the solvent was made to dissolve or distribute, and moreover, this solution needs to be a thing with low surface tension to such an extent that it wets PTFE. For this reason, since this ink-like solution becomes what can also wet gas diffusion layer material, When forming a catalyst bed on a gas diffusion layer material face, the part, especially solid polymer electrolyte pitch of an ink component may permeate a gas diffusion layer, For this reason, when the water repellence of a gas diffusion layer fell, for

example, it was made to operate as a fuel cell, catalyst surfaces got wet with the moisture to generate, and gas diffusion might worsen and, as a result, might cause degradation.
[0010]This invention solves these problems, have uniform thickness and high intensity, and The polymers solid electrolyte thin film of necessary minimum thickness moreover, Have combined with this firmly and electrical-and-electric-equipment (ion conduction) contact moreover is also fully secured, Therefore, with gas diffusion nature movement of generation ion is also performed promptly and good and high reactivity. The polymers solid-electrolyte membrane / electrode conjugate which comprises the catalyst bed of high intensity are proposed, and the electrode / polymers solid-electrolyte membrane / electrode conjugate which has an electrode also in the opposite side which sandwiches the polymers solid-electrolyte membrane of this zygote further are also proposed.
[0011]
[Means for Solving the Problem]On namely, the surface of a compound polymers solid-electrolyte membrane as for which this invention consists of extension porosity polytetrafluoroethylene and solid polymer electrolyte resin contained in the porosity hole part. A compound polymers solid-electrolyte membrane / electrode integral-moulding object, wherein an electrode filled up with an electrode configuration ingredient which contains an electrode catalyst and a solid polymer electrolyte at least all over an opening of extension porosity PTFE is formed in one, And the electrode / compound polymers solid-electrolyte membrane / electrode integral-moulding object which formed in both sides of the above-mentioned compound polymers solid-electrolyte membrane at one an electrode filled up with an electrode configuration ingredient which contains an electrode catalyst and a solid polymer electrolyte at least all over an opening of extension porosity PTFE, respectively are provided.
[0012]After this invention arranges the 1st extension porosity polytetrafluoroethylene similarly on a substrate which has a mold-release characteristic, by applying a solution of solid polymer electrolyte resin to the surface, Solid polymer electrolyte resin is impregnated all over an opening of extension porosity polytetrafluoroethylene, Remove a solvent, form a compound polymers solid-electrolyte membrane, and the 2nd extension porosity polytetrafluoroethylene membrane is succeedingly arranged on the surface, By applying to the surface an ink-like solution which contains an electrode catalyst and solid polymer electrolyte resin at least, After an ink-like solution is impregnated all over an opening of the 2nd extension porosity polytetrafluoroethylene, After obtaining an electrode by forming it in the polymers solid-electrolyte membrane surface by removing a solvent, A process of the compound polymers solid-electrolyte membrane / electrode integral-moulding object removing a substrate which has a mold-release characteristic and acquiring a compound polymers solid-electrolyte membrane / electrode integral-moulding object, And by applying a solution of solid polymer electrolyte resin to the surface, after arranging the 1st extension porosity

polytetrafluoroethylene on an electrode fabricated beforehand, Solid polymer electrolyte resin is impregnated all over an opening of extension porosity polytetrafluoroethylene, remove a solvent, and a compound polymers solid-electrolyte membrane is formed, By arranging the 2nd extension porosity polytetrafluoroethylene membrane on the surface succeedingly, and applying to the surface an ink-like solution which contains an electrode catalyst and solid polymer electrolyte resin at least, After an ink-like solution is impregnated all over an opening of the 2nd extension porosity polytetrafluoroethylene, a process of the electrode / composite high polymer electrolyte film / electrode integral-moulding object forming an electrode in the compound polymers solid-electrolyte membrane surface is provided by removing a solvent.

[0013]Extension porosity PTFE (it abbreviates to EPTFE henceforth) used by this invention is a three-dimensional network structure thing which consists of a PTFE microfilament which connects these with a minute tubercle of countless PTFE mutually so that may be indicated to JP,51-18991,B. According to manufacturing conditions, the physical properties and structure are controllable and can provide a high intensity structure considering height of voidage. Although various kinds of things can be used as solid polymer electrolyte (it abbreviates to PE henceforth) resin according to a use, it dissolves, for example with a polyethylene oxide alkali-metal-salt complex and various organic electrolysis liquid, and the rubbers which can be held are mentioned. As an object for fuel cells, perphloro sulfonate resin and ion-exchange resin of various hydrocarbon systems and a fluorine system are used. A catalyst of platinum etc., carbon powder, and various ceramic powder may be added in the range which electron conductivity does not produce to this PE resin depending on the case.

[0014]Generally as a solvent of these resin solutions, an organic solvent of various hydrocarbon systems, water, or these partially aromatic solvents are used. What is necessary is for an EPTFE film to be hard to be impregnated depending on a molecular weight of resin, or a kind of solvent, when PE resin solution is impregnated or spreading impregnated, but just to carry out suitably suitable processing of addition of concentration adjustment, a surface-active agent, or a solvent with low surface tension, a surface treatment of an EPTFE film, etc. in this case.

[0015]Although a compound PE film which is thin and has high intensity in this invention by impregnating solid polymer electrolyte resin all over an opening of this EPTFE is obtained, It may not limit especially as the method and may carry out by removing a solvent, after carrying out dipping of the EPTFE film, for example to PE resin solution, A solvent may be removed and created, after apply to the surface with a brush etc., or applying with screen printing, or applying by a roll coater etc. and being impregnated. When it is hard to be impregnated, operation which is rubbed mechanically, and physical operation on which an ultrasonic wave is made to act may be performed. Of course, it repeats several times, and it may be impregnated and this may be created. In this case, a layer of only PE resin may be made on the surface of

bipolar membrane of EPTFE and PE resin, and it does not matter even if a part of EPTFE is exposed in layers, and an imperforate layer should just be formed continuously. Although suitable methods, such as air-drying or stoving, may be used for removal of a solvent, it is necessary to avoid excessive heating which causes decomposition of PE. If required intensity and thickness are filled as EPTFE used here, Since membrane resistance becomes low as a thing with high voidage, it is desirable, but generally From 1 micrometer of thickness to 100 micrometers. The aperture can use [micrometer / 0.05] 5 micrometers of 0.5 to 2-micrometer things 80% to 95% about 98% from 2 micrometers to 30 micrometers, and 60% of voidage preferably.

[0016]Various impalpable powder, such as ceramic powder, such as conductive powder, such as catalyst powder, such as platinum, carbon black, and black lead, and alumina, etc. may be included in the range which electron conductivity does not produce in this EPTFE depending on the case. In this case, a homogeneous-mixing raw material of PTFE and these impalpable powder is prepared, and the rest is obtained by processing it like a PTFE simple substance raw material.

[0017]An electrode which an electrode configuration ingredient which contains an electrode catalyst and PE at least all over an opening of EPTFE is filled up with this invention into the surface of a compound solid polymer electrolyte resin layer produced by making it above, and changes is formed in one. As physical properties and structure of having been suitable for EPTFE used here, 3-200 micrometers of thickness, not less than 60% of voidage, and an aperture are EBP values (although it is a method given in ASTM;F-316-86 and becomes a rule of thumb of the maximum aperture). EPTFE does not compute the maximum aperture as it is for fibril structure. It is below 0.5 kg / cm^2. Although optimal thickness changes with required catalyst amounts and demand characteristics, in less than 3 micrometers, securing a required catalyst amount cannot secure a place of three-dimensional reaction difficult and sufficient again. At more than 200 micrometers, gas diffusion nature and ion conductivity have trouble, and a catalyst does not function enough. At less than 60%, the amount of PTFE increases relatively, resistance will not change low enough and void content of a catalyst amount with which it can be filled up will decrease. It is difficult for aperture of an aperture to be too small in 0.5 kg/cm^2 ** at an EBP value, and to fill up a cavity part in a film with a catalyst particle. Although structure where a minute pars tuberalis is small as much as possible, and structure which will consist only of microfilament if possible are preferred, it is not limited to this. While becoming possible to be filled up with material which begins by using such an EPTFE film and contains PE and a catalyst component in the cavity part, a required catalyst amount, While being able to function as an electrode which could secure gas diffusion nature and conductivity (ion and electron), therefore was excellent, a uniform catalyst bed can be obtained with sufficient reproducibility according to a reinforcing effect by an EPTFE fibril network, and a

matrix effect of EPTFE.

[0018]As this EPTFE, a conductive material, for example, carbon black, graphite powder, titanium powder that carried out the coat of the platinum, etc. may be included in that material texture. Of course, the catalyst itself or a thing which supported a catalyst may be sufficient as this powder. Thus, in order to create EPTFE which contains such impalpable powder in material texture, Material which removed and ground back moisture made to coagglutinate after mixing dispersion liquid which made dispersion of PTFE distribute these powder, and was made powdered can be prepared, and this can be processed and obtained according to a method of an indication to JP,51-18991,B like material of PTFE.

[0019]Restoration of an ingredient to a cavity part of EPTFE which includes solid polymer electrolyte resin and a catalyst at least is performed by removing a solvent, after an EPTFE cavity part is impregnated in a mixed solution containing these ingredients. or [that solid polymer electrolyte resin can dissolve as a solvent of this solution although these mixed solutions, such as a water + surface-active agent and an organic solvent, are used] -- or it is necessary to stabilize and distribute

[0020]Although what was used for said compound PE film is preferred as solid polymer electrolyte resin, it does not adhere to in particular this and ion-exchange resin of a hydrocarbon system or a fluorine system can use it arbitrarily. Ion-exchange resin, especially perphloro sulfonate resin of a perphloro carbon system are preferred the optimal. This resin can be obtained with a trademark of "Nafion" for example, from U.S. Du Pont. A mixed solvent of an organic solvent [solvent / of a solution of this resin] centering on various alcohols, or this and water is used.

[0021]Arbitrary powder which acts as an electrode catalyst can use a catalyst according to a use. For example, in an ozone generating electrode, it is platinum or a platinum metal metal alloy at anhydrous plumbic acid and a water electrolysis electrode, and they are platinum or platinum alloy support carbon black in a fuel cell. A mixed solution of this catalyst powder and solid polymer electrolyte resin is producible by adding a solid polymer electrolyte resin solution, after making the above-mentioned solvent distribute catalyst powder. A hole is made and it may be made to improve gas diffusion nature further by strengthening water repellence, or adding ostomy agents, such as ammonium bicarbonate, salt, and calcium carbonate, and removing after shaping by furthermore adding PTFE dispersion or FEP dispersion depending on the case.

[0022]It can be a mixed solution of a solution and conductive powder which contain solid polymer electrolyte resin and a catalyst precursor as solid polymer electrolyte resin and a mixed solution including a catalyst. Namely, by adding a positive ion of catalyst metal which can be combined with this exchange group when cation exchange resin is used as solid polymer electrolyte resin, It may be the mixed solution of resin, conductive powder, and solid

polymer electrolyte resin which combined a positive ion of catalyst metal with solid polymer electrolyte resin. After having used carbon black as conductive powder, making a solid polymer electrolyte resin solution specifically distribute this and making solid polymer electrolyte resin stick to carbon black, What is necessary is to add a solid polymer electrolyte resin solution further, and just to adjust an ink-like solution, after adding and carrying out ionic exchange of a positive ion, for example, a platinum ammine complex solution, of catalyst metal. It may be the thing which mixed these simultaneously, of course. When such a solution is used, after forming a film / electrode or an electrode / film / electrode integral-moulding object by this invention, it is necessary to change a catalyst precursor into a catalyst by reduction processing of some kind. What is necessary is to just be based on suitable methods, such as warm water matter reduction processing and chemicals reduction by sodium borohydride etc., as this reduction processing. A high catalyst of activity can be acquired by using such a solution.

[0023]It can also carry out by only applying to a film surface a solution produced by making it above, in order to impregnate EPTFE. It may be made to push in into an EPTFE film mechanically by letting this pass on a roll etc. further. By mixing a solid polymer electrolyte resin solution with this catalyst, by operation of solidification by being impregnated and solvent removal, while covering a catalyst with solid polymer electrolyte resin, A role of a binder which solid polymer electrolyte resin makes catalyst particles bind, and fixes a catalyst on internal net eye structure of an EPTFE film is achieved, A role of a junction binder with said compound PE film is achieved, and a passage to which ion generated on a catalyst particle is promptly moved to a polymers solid-electrolyte membrane is formed.

[0024]According to this invention, since a mechanical strength of a catalyst bed is based on an EPTFE film matrix, a mechanically stable catalyst bed can be formed with necessary minimum solid polymer electrolyte resin, therefore inhibition of gas diffusion nature by superfluous solid polymer electrolyte resin can be prevented. When a solvent is furthermore removed from this mixed solution, a formed element condenses and volume becomes small, but. According to this invention, since cohesive force is distributed by fibril matrix of EPTFE, at the time of condensation contraction, the amount of [a volumetric shrinkage or] void volume will form fine gaps as it is, and it becomes a good structure of gas diffusion nature. Since solid polymer electrolyte resin itself is continuing, movement of ion is performed smoothly and electrode performance outstanding as a result is provided.

[0025]In this invention, junction on a catalyst bed and a compound PE film is also simultaneously performed by performing formation of this catalyst bed on a compound PE film which was able to be obtained from EPTFE and PE solution. Such a thing is beginning with combination of this catalyst bed and this compound PE, and becoming possible, for example, even if it forms this catalyst bed by operation that generally it is the same on PE film by

available thermofusion shaping, unless heat and a pressure are fully put after that, it cannot obtain sufficient bonding strength. Since PE of a compound PE film and PE in a catalyst bed are continuing in a zygote of this invention, It is possible for movement of ion to be performed smoothly, for there to be no osmosis of superfluous PE resin to an electrode, while electrode performance outstanding as a result is provided, for an electrode which continues being a predetermined electrode component to be formed, and for it to be stabilized with sufficient reproducibility and to produce a highly efficient electrode.

[0026]When same operation is performed without an EPTFE film here using a film which only obtained it by carrying out the cast of the PE resin solution, It is difficult for PE film to dissolve, or to swell violently, and for a crack etc. to occur at the time of solvent removal it not only to be unable to to form a catalyst bed well, but, and to form a zygote with a solvent of an ink-like solution used at the time of catalyst bed formation. This becomes more difficult at the time of thin PE film especially. Conversely, even if it uses this PE film and is going to form a catalyst bed by applying an ink-like solution without an EPTFE film at the time of catalyst bed formation directly, it will be the catalyst bed which crocodiled violently with cohesive force at the time of solvent removal, and will be a thing inferior to performance as an electrode.

[0027]When performing this operation, may carry out on an independent compound PE film, but more preferably, . A compound PE film is formed and it is made to perform this operation on that surface on a substrate which has a mold-release characteristic continuously. Namely, after arranging the first EPTFE on a substrate which has a mold-release characteristic, PE solution is impregnated all over an opening of EPTFE by applying PE solution to the surface, After forming a catalyst bed in the surface further like an account of Gokami which removed a solvent and formed a compound PE film, it is preferred to remove a substrate which has a mold-release characteristic and to acquire the compound PE film / electrode integral-moulding object of this invention.

[0028]Even if it is put to a solvent of PE at the time of catalyst bed formation of a next process by forming a compound PE film on a substrate which has a mold-release characteristic, swelling to a plane direction can be suppressed nearly thoroughly, and can form a more uniform and highly efficient catalyst bed, and. Since a compound PE film can be treated by a substrate and one, when especially a compound PE film is thin, the handling becomes it is remarkable and easy.

[0029]As a substrate which has a mold-release characteristic, a zygote of this invention can be exfoliated eventually, and swelling etc. are not remarkably caused to a solvent at the time of zygote formation of this invention, and what is necessary is that what is necessary is just to just have the surfaces, such as polyethylene, polypropylene, silicon, and various fluoro-resins. In order to use a zygote obtained by this invention for an electrochemical device, Prepare PE film independently, and a zygote of this invention is doubled with both sides of this film as a

compound PE film faces this PE film, Although it is good also as an electrode / film / an electrode conjugate by carrying out heat pressing to join, more preferably, a compound PE film surface is opposed, the zygotes of this invention are joined, and an electrode / film / electrode conjugate is obtained. In a zygote of this invention, since a compound PE film is formed from a solution, it can excel in an adhesive property dramatically, for example, can paste up easily by heat pressing operation on short-time comparatively quiet conditions considerably like a heat roll, and what moreover has sufficient adhesive strength can be produced. Even if a solvent is removed and it joins after dissolving the surface, making each other face too succeedingly and comparing as an option by applying only PE solution or its solvent to the surface of at least one compound PE film, a zygote which has sufficient adhesive strength is producible. Especially these methods are begun by using this invention integral-moulding object for at least one electrode, when it is going to make PE film thin, and become possible, and by a film by commercial thermofusion shaping, even if it performs same operation, sufficient bonding strength is not obtained. It softens, and when it lets a heat roll pass, intensity will fall extremely, and it will be torn, inter-electrode will connect too hastily, or thickness will change or differ extremely in what is depended on cast film production of only PE resin which does not contain EPTFE, and will become what has low reliability in it. It swells thru/or dissolves and stable junction is difficult what adhesive strength is not obtained by a commercial film even if it applies PE resin solution similarly, and is depended on cast film production.

[0030]This invention proposes an electrode / film / electrode conjugate further. Namely, after extension porosity PTFE is impregnated in a solid polymer electrolyte solution, At least on one side of a compound polymers solid-electrolyte membrane obtained by removing a solvent. They are an electrode / compound polymers solid-electrolyte membrane / electrode integral-moulding object, wherein an electrode which it fills up with an electrode configuration ingredient which contains an electrode catalyst and a solid polymer electrolyte at least all over an opening of extension porosity PTFE, and changes is fabricated by one. After such a product arranges 1st extension porosity PTFE on an electrode fabricated beforehand, by applying a solution of a solid polymer electrolyte to the surface, A solid polymer electrolyte is impregnated all over an opening of extension porosity PTFE, remove a solvent, and a compound polymers solid-electrolyte membrane is formed, By arranging the 2nd extension porosity PTFE film on the surface succeedingly, and applying to the surface an ink-like solution which contains an electrode catalyst and a solid polymer electrolyte at least, After an ink-like solution is impregnated all over an opening of 2nd extension porosity PTFE, an electrode can be obtained by the ability to form it in the compound polymers solid-electrolyte membrane surface by removing a solvent.

[0031]Here, if it is an electrode used for an electrochemical device which uses PE film as an electrode fabricated beforehand, all are applicable, but since an adhesive property with a

compound PE film is increased, it may be necessary to apply PE solution beforehand. Although what carried out being spreading impregnated of the PE resin is mentioned to a thing which bound various catalyst powder with resin, such as PTFE, or this surface as such an electrode, On a substrate which has a mold-release characteristic, or what is called a gas diffusion layer material face that is conductivity and has water repellence, an electrode applied, dried and obtained is [the above-mentioned ink-like solution] preferred more preferably, and it especially, An electrode which it fills up with an electrode configuration ingredient which contains an electrode catalyst and PE resin at least all over an opening of EPTFE the same with having mentioned above on a substrate which has a mold-release characteristic, or a gas diffusion layer material face, and changes is preferred. When a zygote of the electrode / film / electrode of this invention is constituted after constituting an electrode on a substrate which has a mold-release characteristic, of course, after constituting this, it is same with having mentioned above to remove this substrate at the end, but when constituted on a gas diffusion layer material face, it will be used as it is.

[0032]According to this invention, a zygote of an electrolyte membrane/electrode or a zygote of an electrode / electrolyte membrane / electrode can be obtained as it understands by the above explanation, but in this invention, junction on a ** (**) ** object may also be performed further simultaneously. When fabricating to this ** (**) ** object and one, after fixing on a ** (**) ** object which is later mentioned before removing a solvent yet after performing above-mentioned being impregnated, or a gas diffusion layer material face, by removing a solvent by air-drying etc., With cohesive force of a solvent and solid polymer electrolyte resin, it joins and unifies by using solid polymer electrolyte resin as a binder. After fixing an EPTFE film as another unification forming process on a ** (**) ** object or a gas diffusion layer material face, After a solution is impregnated all over an opening of EPTFE by applying the above-mentioned mixed solution or letting this pass on a roll etc. further, air-drying etc. can remove a solvent, and it can also join and unify.

[0033]Also in which above method, it may be necessary to stabilize resin by heating or other means eventually a kind of solid polymer electrolyte resin. An organizer is [of this invention / the compound (electrode/) polymers solid-electrolyte membrane / really / electrode] shown in drawing 1 (A) and (B). One is a compound polymers solid-electrolyte membrane and an electrode configuration ingredient in which a minute tubercle of EPTFE of a polymers solid-electrolyte membrane and 4 contain a microfilament of EPTFE in, 5 contains a solid polymer electrolyte in, and, as for 2, 6 contains an electrode catalyst and a solid polymer electrolyte at least, as for an electrode and 3 among drawing 1.

[0034]Generally, in a use of a zygote of the electrolyte membrane/electrode of this invention, in many cases, it is used with a charge collector or a feeding body, and, especially in the case of a fuel cell, a conductive water-repellent gas diffusion layer is further provided in the meantime

in many cases. As a **(** ** object, that with which gold and a platinum group plated or coated mesh, such as nickel, titanium, copper, and stainless steel, an expanded mesh, or these metal meshes, porous carbon or graphite, carbon paper, etc. are used.

[0035]What [gave the thing same as a water-repellent gas diffusion layer as material of the above-mentioned collection (**) ** object a water-repellent finish by PTFE], What mixed conductive powder, such as PTFE, carbon black, or black lead, and was fabricated with a press etc. on the above-mentioned collection (**) ** object at one, There are what was made into paste state, was applied, carried out dry calcination, and was fabricated, a thing which was kneaded and was fabricated to a sheet shaped, a thing which extended this further and raised porosity more, etc.

[0036]The method of using the electrolyte membrane/electrode conjugate of this invention like the above for various kinds of electrochemical devices can be the same as usual except using the electrolyte membrane/electrode of this invention. An example of a fuel cell is shown in drawing 2. As for a ** (**) ** object, and 9 and 10, a solid polymer electrolyte and 2 are [a gas supplying groove and 13] gas diffusion layer sheets a separator board, and 11 and 12 an electrode, and 7 and 8 one among drawing 2. A zygote of solid polymer electrolyte 1 / electrode 2 of this invention or a zygote of electrode 2 / solid polymer electrolyte 1 / electrode 2 can be used as a zygote with a ** (**) ** object if needed.

[0037]In this way, in a constituted polymers solid electrolyte fuel cell. If drawing 2 is referred to, O_2 will be supplied to the gas supplying groove 28 and H_2 will be supplied to the slot 29, Within the electrode 22, $O_2+4H^++4e^- \rightarrow 2H_2O$, A reaction of $2H_2 \rightarrow 4H^++4e^-$ occurs within the electrode 23, $4H^+$ flows into the electrode 22 from the electrode 23 through the solid polymer electrolyte 21, and $4e^-$ becomes electrical energy by passing along external load. About 100 ** of operating temperature is about 80 ** preferably from 60 **.

[0038]The electrolyte membrane/electrode of this invention can be used for a water electrolysis system, an ozone generator besides a polymers solid electrolyte fuel cell, etc.

[0039]

[Example]

After 10 micrometers of thickness, 83% of voidage, and the maximum aperture fix the EPTFE film of 1.75 kg / cm^2 to the surface of an example 1PP sheet with an EBP value, After the cavity part of the EPTFE film was impregnated by applying concentration 5wt% of a perfluoro sulfonic acid resin solution to the surface, by being air-dry at 70 **, the solvent was removed and resin was fixed in the film. By repeating this operation 4 times, impregnating immobilization of the resin was fully carried out at the cavity part of the EPTFE film, and the almost transparent compound polymers solid-electrolyte membrane was obtained. At this time, this compound polymers solid-electrolyte membrane has adhered to PP sheet enough.

It was in the state which can be dealt with as a sheet of about one body.

[0040]this -- another -- platinum -- 30wt% -- the concentration 10wt% ink-like solution so much mixed at a rate of the perfluoro sulfonate resin 1 was prepared for the supported carbon black (it abbreviates to PtC henceforth) 3. On next, the compound polymers solid-electrolyte membrane surface of PP sheet / compound polymers solid-electrolyte membrane prepared previously. After 10 micrometers of thickness, 91% of voidage, and the maximum aperture fix the EPTFE film of 0.13 kg / cm^2 with an EBP value, by applying said ink-like solution to the surface, The cavity part of this EPTFE film was impregnated in the ink-like solution, by being air-dry at 70 **, the solvent was removed and the catalyst bed of the form which PtC and solid polymer electrolyte resin related for which and attached to an EPTFE film cavity part and the internal structure surface on the compound solid polymer electrolyte surface was formed in one. Then, this integral-moulding object was removed from PP sheet, and the compound polymers solid-electrolyte membrane / electrode integral-moulding object of this invention were acquired.

[0041]By letting it pass between the rolls of the couple heated at 150 **, after making two sheets and a compound solid polymer electrolyte side associate and piling up the integral-moulding object acquired in example 2 Example 1, carry out thermal melting arrival and another [an air pole and] field is made into a hydrogen pole for one field, After having arranged the carbon paper which inserted with the gas diffusion layer sheet which consists of carbon black and PTFE like drawing 2, and gave the outside a water-repellent finish by PTFE further, the fuel cell was constituted by holding down with a ribbed separator board. And when this fuel cell was made to generate, the output of 0.64V was obtained with the current density of 0.5A/cm^2. The AC resistance values at this time are about 0.07 ohm and cm^2, and these values hardly changed even after 800-hour operation.

[0042]Used the thing of 6 micrometers of thickness as an EPTFE film fixed on PP sheet in example 3 Example 1, it made to be spreading impregnated of solid polymer electrolyte resin into 2 times, and also the compound polymers solid-electrolyte membrane / electrode integral-moulding object of this invention were acquired similarly. Next, it has arranged so that the perfluoro sulfonic acid film by the melt molding of 50 micrometers of thickness prepared independently may be carried out in between and a two-sheet compound polymers solid-electrolyte membrane side may face the integral-moulding object of this invention each other, and it joined to one by carrying out a hotpress by the pressure of 140 **, and 30 kg / cm^2. The fuel cell was constituted like Example 2 using this zygote, and when oxygen water matter was made to supply and generate, the output of about 0.6 v was obtained with the current density of 1 A/cm2.

[0043]By arranging the EPTFE film of 91% of the same 10 micrometers of thickness voidage as having used it in Example 1 on PP sheet of 70 micrometers of example 4 thickness, and applying the same ink-like solution as having used it in Example 1 to the surface, It was impregnated in the EPTFE film, the solvent was removed, and the electrode which the mixture of PtC and solid polymer electrolyte resin contained was formed all over the EPTFE film opening. This electrode had adhered on PP sheet well.

[0044]Then, after having arranged the EPTFE film of 85% of 18 micrometers of thickness voidage on this surface, concentration 9wt% of the perfluoro sulfonic acid resin solution was applied to that surface, and it was further air-dry at 70 ** succeedingly on it. Impregnating immobilization of the perfluoro sulfonate resin was carried out all over this EPTFE film opening, and the compound polymers solid-electrolyte membrane was made to form on an electrode surface by repeating this process 5 times at one.

[0045]Next, arrange 10 micrometers of the same thickness as having used it for this surface previously further, and the EPTFE film of 91% of voidage, and too the same ink-like solution spreading, being impregnated, and by carrying out solvent removal, After forming in one the electrode which the mixture of PtC and solid polymer electrolyte resin contained all over this EPTFE film opening on the compound polymers solid-electrolyte membrane and forming an electrode / compound polymers solid-electrolyte membrane / electrode integral-moulding object on PP sheet, it removed from PP sheet and this invention integral-moulding object was acquired.

[0046]When the hydrogen-air fuel cell was constituted like Example 2 and the integral-moulding object acquired in example 5 Example 4 was made to generate, the output of 0.62V was obtained with the current density of 0.5A/cm^2, and the AC resistance values at this time were 0.065 ohm and cm^2.

[Translation done.]

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(71)出願人　000107387
ジャパンゴアテックス株式会社
東京都世田谷区赤堤１丁目42番５号

(72)発明者　加藤　博
東京都世田谷区赤堤１丁目42番５号　ジャパンゴアテックス株式会社内

(74)代理人　弁理士　石田　敬　（外３名）

(54)【発明の名称】高分子固体電解質膜／電極一体成形体及びその製法

(57)【要約】

【目的】　均一な膜厚及び高強度で必要最低限の厚さの高分子電解質膜と、これと強固に結合し電気的接触が確保された高強度の触媒層とを一体化した高分子固体電解質／電極接合体を提供すること。

【構成】　高分子固体電解質樹脂溶液を延伸多孔質ＰＴＦＥに含浸した後、溶媒を除去して得られた複合高分子固体電解質膜の表面に、延伸多孔質ＰＴＦＥの空隙中に、少なくとも電極触媒と高分子固体電解質を含む電極構成成分が充填されて成る電極が一体に成形されていることを特徴とする複合高分子固体電解質膜／電極一体成形体。

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【特許請求の範囲】

【請求項１】　延伸多孔質ポリテトラフルオロエチレンとその多孔質空孔部に含有された高分子固体電解質樹脂とからなる複合高分子固体電解質膜の表面に、延伸多孔質ＰＴＦＥの空隙中に少なくとも電極触媒と高分子固体電解質を含む電極構成成分を充填して成る電極が一体に形成されていることを特徴とする複合高分子固体電解質膜／電極一体成形体。

【請求項２】　離型性を有する基材上に第１の延伸多孔質ポリテトラフルオロエチレンを配置した後、その表面に高分子固体電解質樹脂の溶液を塗布することにより、延伸多孔質ポリテトラフルオロエチレンの空隙中に高分子固体電解質樹脂を含浸し、溶媒を除去して複合高分子固体電解質膜を形成し、引き続いてその表面に第２の延伸多孔質ポリテトラフルオロエチレン膜を配置し、その表面に、少なくとも電極触媒と高分子固体電解質樹脂とを含むインク状溶液を塗布することにより、第２の延伸多孔質ポリテトラフルオロエチレンの空隙中にインク状溶液を含浸した後、溶媒を除去することにより電極を高分子固体電解質膜表面に形成して得た後、離型性を有する基材を除去して複合高分子固体電解質膜／電極一体成形体を得ることを特徴とする複合高分子固体電解質膜／電極一体成形体の製法。

【請求項３】　延伸多孔質ポリテトラフルオロエチレンとその多孔質空孔部に含有された高分子固体電解質樹脂とからなる複合高分子固体電解質膜の表面に、延伸多孔質ＰＴＦＥの空隙中に少なくとも電極触媒と高分子固体電解質を含む電極構成成分を充填して成る電極が一体に形成され、かつ該複合高分子固体電解質膜のもう１つの表面にも電極が一体化されていることを特徴とする電極／複合高分子固体電解質膜／電極一体成形体。

【請求項４】　前記複合高分子固体電解質膜の両面に、延伸多孔質ＰＴＦＥの空隙中に少なくとも電極触媒と高分子固体電解質を含む電極構成成分を充填して成る電極がそれぞれ一体に形成されている請求項３記載の電極／複合高分子固体電解質膜／電極一体成形体。

【請求項５】　予め成形された電極上に第１の延伸多孔質ポリテトラフルオロエチレンを配置した後、その表面に高分子固体電解質樹脂の溶液を塗布することにより、延伸多孔質ポリテトラフルオロエチレンの空隙中に高分子固体電解質樹脂を含浸し、溶媒を除去して複合高分子固体電解質膜を形成し、引き続いてその表面に第２の延伸多孔質ポリテトラフルオロエチレン膜を配置し、その表面に少なくとも電極触媒と高分子固体電解質樹脂とを含むインク状溶液を塗布することにより、第２の延伸多孔質ポリテトラフルオロエチレンの空隙中にインク状溶液を含浸した後、溶媒を除去することにより電極を複合高分子固体電解質膜表面に形成することを特徴とする電極／複合高分子電解質膜／電極一体成形体の製法。

【請求項６】　請求項５において、予め成形された前記電極を、離型性を有する基材上に、少なくとも電極触媒と高分子固体電解質樹脂とを含むインク状溶液を塗布した後、溶媒を除去することにより得ることを特徴とする電極／複合高分子電解質膜／電極一体成形体の製法。

【請求項７】　請求項５において、予め成形された前記電極を、離型性を有する基材上に、延伸多孔質ポリテトラフルオロエチレン膜を配置し、その表面に、少なくとも電極触媒と高分子固体電解質樹脂とを含むインク状溶液を塗布して、延伸多孔質ポリテトラフルオロエチレンの空隙中にインク状溶液を含浸した後、溶媒を除去することにより得ることを特徴とする電極／複合高分子電解質膜／電極一体成形体の製法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は高分子固体電解質／電極接合体に係わる。より詳しくは、イオン導電性高分子固体電解質を使用する電気化学装置の電極／高分子固体電解質接合体に係わり、例えば、リチウムイオン伝導性固体電解質を使用したリチウムが電池或いはプロトン伝導性固体電解質を使用した水電解装置等に利用し得るが、最適にはプロトン伝導性固体電解質を使用する高分子固体電解質型燃料電池に使用するものである。

【０００２】

【従来の技術】高分子固体電解質を使用した電気化学装置ではエネルギー効率の一層の向上が求められており、そのため電極構造を工夫し、電極反応点を三次元化して反応活性点を増す様にすると共に高分子固体電解質を電極内部にも配置し、速やかにイオンが移動できる様にしている。発生したイオンを速やかに対極まで移動できる様にするためには、電極内の固体電解質と隔膜である固体電解質膜との接触が良く、又固体電解質膜自体の膜抵抗が低い必要があり、そのためには膜厚はできるだけ薄い方が好ましい。更に、燃料電池で使用されている高分子固体電解質膜は常に湿潤状態で使用しなければイオン伝導性の低下や、分極が発生して性能が低下するため、反応ガスに加湿して、間接的に湿潤状態を維持するようにしているが、高分子固体電解質膜が薄いほど加湿効率が良く、限界電流密度の向上が期待できる。

【０００３】また、従来は、固体電解質膜と電極をそれぞれ別に用意し、これらを重ね合わせた後ホットプレスにより接合する方法が一般的に行われており、高分子固体電解質としては市販品として膜状に成形されたもの（例えば米国デュポン社製ナフィオン＃１１５等）や、その溶液をキャストして薄膜状に成形したもの等が使用されている。またホットプレスせずに機械的にはさみこんで使用することも提案されている。

【０００４】

【発明が解決しようとする課題】しかしながら、ホットプレスによる接合に於いては、温度により膜が軟化したところで圧力が加えられるため、膜厚をあまり薄くする

と膜が破壊されて、ガス漏れを生じたり、電極間の短絡が発生したりしやすいという問題があった。このことは電極の平滑性が悪いときには更に難しい問題となるため、極端に膜厚を薄くすることは困難であった。またホットプレス時に電極自体も圧密化されるため、高電流密度での作動を可能にするための電極の重要な要素である通気性を損なうという問題もあった。

【０００５】これら等の問題を解決し、またホットプレス工程そのものを省略できるということで、機械的にはさみこんで使用する方法も提案されているが、電極との接触を一様に保つこと及び接触抵抗自体を低く保つためには、かなりの圧力を必要とし、膜厚を薄くした場合、ホットプレスと同様の問題があった。また複数セルを積み重ねて構成される燃料電池に於いては、電極または膜の応力緩和等により長期にわたって一定の接触抵抗を保つことは困難であり信頼性の低いものになってしまう。

【０００６】これらの問題を解決する為に、電極触媒、好ましくはシート状に成形された電極または電極触媒面上に、高分子固体電解質樹脂の溶液を塗布乾燥することにより直接固体電解質膜を形成して接合体とし、更にこの様にして成形された接合体どうしを固体電解質膜面をつき合わせてホットプレスするか、または高分子固体電解質樹脂溶液またはその溶媒を塗布した後つき合わせて一体化した後溶媒を除去するか、または電極面に高分子固体電解質樹脂の溶液を塗布した後未乾燥状態のうちにやはり電極または電極面に高分子固体電解質溶液を塗布または塗布乾燥したものをつき合わせた後、溶媒を除去して陽極／膜／陰極一体成形品とすることも提案されている。しかしながら、電極触媒層面上に高分子固体電解質樹脂溶液を塗布して膜を成形する方法では、電極構造によっては造膜性が悪く、過度に溶液を塗布する必要があり、そのため電極触媒層内への高分子固体電解質樹脂の浸透が過剰になり、ガス拡散性を阻害する可能性があった。また均一な膜厚とすることも難しく、膜厚を薄くしようとする場合、やはり電極間の短絡を生じる可能性が高いものであった。

【０００７】本発明者は、高分子固体電解質膜を使用した電気化学装置の高エネルギー効率、及び高電流密度での作動を可能とすべく、固体電解質膜の厚さを薄くすることを可能とし、しかも電極本来の物性を損なわずに、電極との接触抵抗を低く且つ確実に確保し、また必ずしもヒートプレス行程を必要としない電極／膜接合体または電極／膜／電極接合体として、電極表面に、延伸多孔質ポリテトラフルオロエチレン（以下、ポリテトラフルオロエチレンをＰＴＦＥと略す。）とその多孔質空隙部に含有された高分子固体電解質樹脂とからなる複合高分子固体電解質膜を一体に成形したものを提案している（特願平６－３０３６７２号明細書）。すなわち電極上に延伸多孔質ＰＴＦＥを配置した後、その表面に高分子固体電解質樹脂溶液を塗布することにより、延伸多孔質ＰＴＦＥの空隙部に高分子固体電解質樹脂溶液を含浸し、その後、溶媒を除去することにより、電極表面に複合高分子固体電解質膜を形成すると同時に電極と一体にするものである。

【０００８】しかしながらこの方法においても、電極の物性によっては、表面に塗布した高分子固体電解質溶液が延伸多孔質ＰＴＦＥ膜を透過して電極にしみこむことにより電極の組成を変えてしまい、電極特性に悪影響を及ぼすことがある。またこの現象が部分的に起こった場合電極特性のバラツキや複合高分子固体電解質膜の厚さや抵抗のバラツキを引き起こすことも有り得る。

【０００９】以上のこととは別に、本発明者は高分子固体電解質膜を用いた電気化学装置用の電極として延伸多孔質ＰＴＦＥの空隙に少なくとも高分子固体電解質樹脂と触媒とを含む成分を充填して成る触媒層を提案しており、またこれをガス拡散層材料面上で構成することにより、ガス拡散層／触媒層一体のいわゆるガス拡散電極を提案している（特願平６－３０４９９１号明細書）。しかしこの電極において延伸多孔質ＰＴＦＥの空隙に高分子固体電解質樹脂と触媒を含む成分を充填するためにはこれら成分を溶媒に溶解または分散させたインク状溶液とする必要があり、しかもこの溶液はＰＴＦＥを濡らす程度に表面張力の低い物である必要がある。このためこのインク状溶液はガス拡散層材料をも濡らし得るものとなるため、ガス拡散層材料面上で触媒層を形成するときにインク成分の一部、特に高分子固体電解質樹脂分がガス拡散層に浸透してしまうことがあり、このためガス拡散層の撥水性が低下してしまい、例えば燃料電池として作動させた場合、発生する水分により触媒面が濡れてしまいガス拡散が悪くなり、その結果性能低下を引き起こしてしまうことがあった。

【００１０】本発明は、これら問題点を解決し、均一な膜厚及び高強度を有しており、しかも必要最低限の厚さの高分子固体電解質薄膜と、これに強固に結合しており、しかも電気（イオン伝導）的な接触も十分に確保されており、従って生成イオンの移動も速やかに行われ、ガス拡散性も良く、反応性の高い、高強度の触媒層とから成る高分子固体電解質膜／電極接合体を提案するものであり、さらにはこの接合体の高分子固体電解質膜を挟む反対面にも電極を有する電極／高分子固体電解質膜／電極接合体をも提案するものである。

【００１１】

【課題を解決するための手段】即ち、本発明は、延伸多孔質ポリテトラフルオロエチレンとその多孔質空孔部に含有された高分子固体電解質樹脂とからなる複合高分子固体電解質膜の表面に、延伸多孔質ＰＴＦＥの空隙中に少なくとも電極触媒と高分子固体電解質を含む電極構成成分を充填して成る電極が一体に形成されていることを特徴とする複合高分子固体電解質膜／電極一体成形体、及び、上記複合高分子固体電解質膜の両面に、延伸多孔

質ＰＴＦＥの空隙中に少なくとも電極触媒と高分子固体電解質を含む電極構成成分を充填して成る電極をそれぞれ一体に形成した電極／複合高分子固体電解質膜／電極一体成形体を提供するものである。

【００１２】本発明は、同様に、離型性を有する基材上に第１の延伸多孔質ポリテトラフルオロエチレンを配置した後、その表面に高分子固体電解質樹脂の溶液を塗布することにより、延伸多孔質ポリテトラフルオロエチレンの空隙中に高分子固体電解質樹脂を含浸し、溶媒を除去して複合高分子固体電解質膜を形成し、引き続いてその表面に第２の延伸多孔質ポリテトラフルオロエチレン膜を配置し、その表面に、少なくとも電極触媒と高分子固体電解質樹脂とを含むインク状溶液を塗布することにより、第２の延伸多孔質ポリテトラフルオロエチレンの空隙中にインク状溶液を含浸した後、溶媒を除去することにより電極を高分子固体電解質膜表面に形成して得た後、離型性を有する基材を除去して複合高分子固体電解質膜／電極一体成形体を得ることを特徴とする複合高分子固体電解質膜／電極一体成形体の製法、並びに、予め成形された電極上に第１の延伸多孔質ポリテトラフルオロエチレンを配置した後、その表面に高分子固体電解質樹脂の溶液を塗布することにより、延伸多孔質ポリテトラフルオロエチレンの空隙中に高分子固体電解質樹脂を含浸し、溶媒を除去して複合高分子固体電解質膜を形成し、引き続いてその表面に第２の延伸多孔質ポリテトラフルオロエチレン膜を配置し、その表面に少なくとも電極触媒と高分子固体電解質樹脂とを含むインク状溶液を塗布することにより、第２の延伸多孔質ポリテトラフルオロエチレンの空隙中にインク状溶液を含浸した後、溶媒を除去することにより電極を複合高分子固体電解質膜表面に形成することを特徴とする電極／複合高分子電解質膜／電極一体成形体の製法を提供する。

【００１３】本発明で使用される延伸多孔質ＰＴＦＥ（以後ＥＰＴＦＥと略す）とは、特公昭５１－１８９９１号公報に記載されるようなものであり、無数のＰＴＦＥの微小結節とこれらを相互に連結するＰＴＦＥ微細繊維からなる３次元的網目構造物である。その物性、構造は製造条件により制御可能であり、空隙率の高さの割には高強度な構造物を提供し得る。また高分子固体電解質（以後ＰＥと略す）樹脂としては、用途に応じて各種の物が使用できるが、例えばポリエチレンオキサイドーアルカリ金属塩複合体や各種有機電解液と相溶し保持可能なゴム類が挙げられる。また燃料電池用としてはパーフロロスルフォン酸樹脂や、各種炭化水素系、フッ素系のイオン交換樹脂が用いられる。また場合によってはこのＰＥ樹脂に、電子伝導性の生じない範囲で白金などの触媒やカーボン粉末、各種セラミクス粉末を加えても良い。

【００１４】これら樹脂溶液の溶媒としては一般に各種炭化水素系の有機溶剤、水、あるいはこれらの混合溶剤が使用される。ＥＰＴＦＥ膜にＰＥ樹脂溶液を含浸、あるいは塗布含浸する場合，樹脂の分子量や溶媒の種類によっては含浸しにくいことがあるが，この場合，濃度調整や界面活性剤あるいは表面張力の低い溶剤の添加，ＥＰＴＦＥ膜の表面処理など，適宜適当な処理をすれば良い。

【００１５】本発明においては、このＥＰＴＦＥの空隙中に高分子固体電解質樹脂を含浸することにより薄くて高強度を有する複合ＰＥ膜を得るわけであるが、その方法としては特に限定するものではなく、例えばＰＥ樹脂溶液にＥＰＴＦＥ膜をディッピングした後溶媒を除去することにより行っても良く，刷毛等により表面に塗布したり、スクリーン印刷法により塗布したり、ロールコーター等により塗布して含浸した後、溶媒を除去して作成しても良い。また含浸しにくい場合には、機械的に揉み込むような操作や超音波を作用させるような物理的な操作を施しても良い。もちろんこれを数回繰り返して含浸して作成しても良い。この場合、ＥＰＴＦＥとＰＥ樹脂の複合膜の表面にＰＥ樹脂のみの層ができていても良く、またＥＰＴＦＥの一部が層状に露出していても構わなく、無孔性の層が連続的に形成されていれば良い。また溶媒の除去は風乾または加熱乾燥等適当な方法で構わないが、ＰＥの分解を招くような過度の加熱は避ける必要がある。ここで使用されるＥＰＴＦＥとしては、必要な強度及び膜厚を満たしていれば、空隙率の高い物ほど膜抵抗が低くなるため好ましいが、一般的には膜厚１μｍから１００μｍ、好ましくは２μｍから３０μｍ、空隙率６０％から９８％程度、好ましくは８０％から９５％、孔径は０．０５μｍから５μｍ、好ましくは０．５μｍから２μｍのものが使用できる。

【００１６】更に場合によっては、このＥＰＴＦＥに電子伝導性の生じない範囲で白金などの触媒粉、カーボンブラック、黒鉛等の導電性粉末、アルミナ等のセラミクス粉等の各種微粉末等を含ませても良い。この場合には、ＰＴＦＥとこれら微粉末との均一混合原料を用意し、あとはＰＴＦＥ単体原料と同様に加工することによって得られる。

【００１７】本発明では、以上の様にして得られた複合高分子固体電解質樹脂膜の表面に、ＥＰＴＦＥの空隙中に少なくとも電極触媒とＰＥを含む電極構成成分が充填されて成る電極を一体に形成する。ここで使用されるＥＰＴＦＥに適した物性、構造としては、膜厚３～２００μｍ、空隙率６０％以上、孔径がＥＢＰ値（ＡＳＴＭ；Ｆ－３１６－８６に記載の方法であり、最大孔径の目安となるが、ＥＰＴＦＥはフィブリル構造の為最大孔径をそのまま算出するものではない。）で０．５kg／cm² 以下である。最適な膜厚は必要な触媒量及び要求特性により変化するが，３μｍ未満では必要な触媒量を確保するのが困難でありまた十分な三次元的反応の場を確保できない。２００μｍ超ではガス拡散性、イオン伝導性に支

障があり、触媒が十分機能しない。空孔率が６０％未満では相対的にＰＴＦＥ量が多くなり、抵抗値が十分低く成らず、また充填できる触媒量も少なくなってしまう。孔径がＥＢＰ値で０．５kg／cm² 超では孔径が小さすぎて触媒粒子を膜内空隙部に充填することが困難である。また、できるだけ微小結節部の小さい構造、可能ならば微小繊維のみからなる構造が好ましいがこれに限定されない。この様なＥＰＴＦＥフィルムを使用することによりはじめてその空隙部にＰＥ及び触媒成分を含む材料を充填することが可能となるとともに必要な触媒量、ガス拡散性、導電性（イオン及び電子）を確保でき、したがって優れた電極として機能できるとともに、ＥＰＴＦＥフィブリルネットによる補強効果、及びＥＰＴＦＥのマトリクス効果により、均一な触媒層を再現性良く得ることができる。

【００１８】またこのＥＰＴＦＥとして、その材料肉質に導電性材料、例えばカーボンブラック、黒鉛粉末、白金をコートしたチタン粉末、等を含んでいても良い。もちろんこの粉末が触媒そのもの、または触媒を担持したものでも良い。この様に材料肉質にこれらの微粉末を含むＥＰＴＦＥを作成するには、ＰＴＦＥのディスパージョンにこれら粉末を分散させた分散液を混合後、共凝集させた後水分を除去し、粉砕して粉末状にした材料を用意し、これをＰＴＦＥの材料と同様に特公昭５１－１８９９１号公報に開示の方法に準じて加工して得ることができる。

【００１９】ＥＰＴＦＥの空隙部への少なくとも高分子固体電解質樹脂と触媒を含む成分の充填は、これら成分を含む混合溶液をＥＰＴＦＥ空隙部に含浸した後、溶媒を除去することにより行われる。この溶液の溶媒としては、水＋界面活性剤、有機溶剤等またはこれらの混合溶液が使用されるが、高分子固体電解質樹脂が溶解できるかまたは安定して分散していられるものである必要がある。

【００２０】高分子固体電解質樹脂としては、前記複合ＰＥ膜に使用したものが好ましいが、特にこれにこだわるものではなく、炭化水素系またはフッ素系のイオン交換樹脂が任意に使用し得る。最適にはパーフロロカーボン系のイオン交換樹脂、特にパーフロロスルフォン酸樹脂が好ましい。この樹脂は例えば米国デュポン社より「ナフィオン」の商標で入手できる。またこの樹脂の溶液の溶媒は各種アルコール類を中心とする有機溶剤またはこれと水との混合溶媒が使用される。

【００２１】触媒は、電極触媒として作用する任意の粉末が用途に合わせて使用し得る。例えばオゾン発生電極では、二酸化鉛、水電解電極では白金または白金属金属合金、燃料電池では白金または白金合金担持カーボンブラック等である。この触媒粉末と高分子固体電解質樹脂との混合溶液は、上記溶媒に触媒粉末を分散させた後、高分子固体電解質樹脂溶液を加えることにより作製できる。さらに場合によっては、ＰＴＦＥディスパージョンまたはＦＥＰディスパージョン等を加えることにより撥水性を強化したり、重炭酸アンモニウム、食塩、炭酸カルシウム等の造孔剤を加え成形後に除去することにより孔を作り、ガス拡散性をさらに高めるようにしても良い。

【００２２】また高分子固体電解質樹脂と触媒を含む混合溶液としては、高分子固体電解質樹脂と触媒前駆物質を含む溶液と導電性粉末との混合溶液であることができる。すなわち高分子固体電解質樹脂として陽イオン交換樹脂を使用した場合にはこの交換基に結合できるような触媒金属の陽イオンを加えることにより、触媒金属の陽イオンを高分子固体電解質樹脂に結合させた樹脂と導電性粉末と高分子固体電解質樹脂の混合溶液であっても良い。具体的には、導電性粉末としてカーボンブラックを使用し、これを高分子固体電解質樹脂溶液に分散させてカーボンブラックに高分子固体電解質樹脂を吸着させた後、触媒金属の陽イオン、例えば白金アンミン錯体溶液を加えてイオン交換させた後更に高分子固体電解質樹脂溶液を加えてインク状溶液を調整すれば良い。もちろんこれらを同時に混合した物であっても良い。この様な溶液を使用した場合には、本発明により膜／電極または電極／膜／電極一体成形体を形成した後何らかの還元処理により触媒前駆物質を触媒に変換してやる必要がある。この還元処理としては加熱水素還元処理や、水素化硼素ナトリウム等による化学還元法等の適切な方法によれば良い。このような溶液を使用することにより、活性の高い触媒を得ることができる。

【００２３】以上のようにして得られた溶液をＥＰＴＦＥに含浸するには、また単にフィルム表面に塗布することにより行うこともできる。またこれをさらにロール等に通すことにより機械的にＥＰＴＦＥフィルム中に押し込むようにしてもよい。この触媒と高分子固体電解質樹脂溶液を混合し含浸、溶媒除去による固化の操作により、触媒を高分子固体電解質樹脂で被覆するとともに、高分子固体電解質樹脂が触媒粒子同士を結着させ、またＥＰＴＦＥフィルムの内部網目構造上に触媒を固定するバインダーの役を果たし、更に前記複合ＰＥ膜との接合バインダーの役を果たすと共に触媒粒子上で生成されるイオンを速やかに高分子固体電解質膜まで移動させる通路を形成する。

【００２４】本発明によれば、触媒層の機械的強度はＥＰＴＦＥフィルムマトリクスによるため、必要最小限の高分子固体電解質樹脂により、機械的に安定した触媒層を形成でき、そのため過剰な高分子固体電解質樹脂によるガス拡散性の阻害を防止できる。さらにこの混合溶液から溶媒が除去される際には、固形成分が凝集し、体積が小さくなるが、本発明によれば、ＥＰＴＦＥのフィブリルマトリクスにより凝集力が分散されるため、凝集収縮時に、体積収縮、または溶媒容積分が、そのまま微細

空隙を形成することになりガス拡散性の良い構造となる。また高分子固体電解質樹脂そのものは連続しているため、イオンの移動はスムースに行われ、結果として優れた電極性能を提供する。

【００２５】更に本発明では、この触媒層の形成をＥＰＴＦＥとＰＥ溶液から得られた複合ＰＥ膜上で行うことにより触媒層と複合ＰＥ膜との接合をも同時に行うものである。この様なことは、本触媒層と本複合ＰＥの組み合わせによりはじめて可能となることであり、例えば一般に入手可能な熱溶融成形によるＰＥ膜上で同様の操作により本触媒層を形成しても、その後で熱と圧力を十分にかけない限り十分な接合強度を得ることはできない。また本発明の接合体に於いては複合ＰＥ膜のＰＥと触媒層中のＰＥが連続している為、イオンの移動はスムースに行われ、結果として優れた電極性能を提供するものであると同時に電極への過剰のＰＥ樹脂の浸透が無く、所定の電極成分のままの電極が形成され、高性能の電極を再現性良く安定して作製することが可能である。

【００２６】ここでＥＰＴＦＥ膜無しに、単にＰＥ樹脂溶液をキャストして得た膜を使用して同様の操作を行った場合には、触媒層形成時に使用するインク状溶液の溶媒により、ＰＥ膜が溶解してしまったり、激しく膨潤して、うまく触媒層を形成できないばかりでなく、溶媒除去時にクラック等が発生して、接合体を形成することは困難である。このことは特に薄いＰＥ膜の時にはより困難となる。逆に本ＰＥ膜を使用したとしても、触媒層形成時のＥＰＴＦＥ膜無しにインク状溶液を直接塗布することにより触媒層を形成しようとしても、溶媒除去時の凝集力により、激しくひび割れた触媒層となってしまい、電極としての性能に劣るものとなってしまう。

【００２７】また、この操作を行う場合、単独の複合ＰＥ膜上で行っても良いが、より好ましくは、離型性を有する基材上で複合ＰＥ膜を形成し、続けてその表面にこの操作を行うようにする、すなわち離型性を有する基材上に第一のＥＰＴＦＥを配置した後、その表面にＰＥ溶液を塗布することによりＥＰＴＦＥの空隙中にＰＥ溶液を含浸し、溶媒を除去して複合ＰＥ膜を形成した後上記と同様にして更にその表面に触媒層を形成した後、離型性を有する基材を除去して本発明の複合ＰＥ膜／電極一体成形体を得るのが好ましい。

【００２８】離型性を有する基材上に複合ＰＥ膜を形成することにより、次工程の触媒層形成時にＰＥの溶媒に曝されても、ほぼ完全に面方向への膨潤を抑えることができ、より均一で高性能な触媒層を形成することができると共に、基材と一体で複合ＰＥ膜を扱えるため、特に複合ＰＥ膜が薄い場合、その取扱いが著しく容易となる。

【００２９】離型性を有する基材としては、最終的に本発明の接合体を剥離でき、また本発明の接合体形成時の溶媒に著しく膨潤等をおこさないものであれば良く、例えばポリエチレン、ポリプロピレン、シリコン、各種フッ素樹脂等の表面を有するものであれば良い。本発明により得られた接合体を電気化学装置に使用するには、ＰＥ膜を別に用意し、この膜の両面に本発明の接合体を、複合ＰＥ膜がこのＰＥ膜に向き合うようにして合わせ、ヒートプレスすることにより接合して電極／膜／電極接合体としても良いが、より好ましくは本発明の接合体どうしを、複合ＰＥ膜面を向き合わせて接合して電極／膜／電極接合体を得る。本発明の接合体では複合ＰＥ膜を溶液から形成しているため、非常に接着性にすぐれ、たとえばヒートロールのようにかなり短時間の、比較的穏やかな条件での加熱加圧操作により容易に接着可能で、しかも十分な接着強度を有するものが作製可能である。また別の方法として、少なくとも一方の複合ＰＥ膜の表面にＰＥ溶液またはその溶媒のみを塗布することによりその表面を溶解させ、引き続いてやはり向かい合わせて突き合わせた後溶媒を除去して接合しても、十分な接着強度を有する接合体を作製することができる。これらの方法は、特にＰＥ膜を薄くしようとした場合、少なくとも一方の電極に本発明一体成形体を使用することによりはじめて可能となるものであり、市販の熱溶融成形による膜では同様の操作を行っても十分な接合強度は得られない。またＥＰＴＦＥを含まないＰＥ樹脂のみのキャスト製膜によるものではヒートロールを通したときに、軟化して極端に強度が低下し破れたり、電極間が短絡してしまったり、膜厚が極端に変化あるいはばらついてしまい信頼性の低いものとなってしまう。同様にＰＥ樹脂溶液を塗布しても市販膜では接着力は得られないし、キャスト製膜によるものでは、膨潤ないし溶解してしまい、安定した接合は困難である。

【００３０】また、本発明は、更に電極／膜／電極接合体を提案する。すなわち、高分子固体電解質溶液を延伸多孔質ＰＴＦＥに含浸した後、溶媒を除去することにより得られた複合高分子固体電解質膜の少なくとも片面に、延伸多孔質ＰＴＦＥの空隙中に少なくとも電極触媒と高分子固体電解質を含む電極構成成分が充填されて成る電極が一体に成形されていることを特徴とする電極／複合高分子固体電解質膜／電極一体成形体である。この様な製品は、予め成形された電極上に第１の延伸多孔質ＰＴＦＥを配置した後、その表面に高分子固体電解質の溶液を塗布することにより、延伸多孔質ＰＴＦＥの空隙中に高分子固体電解質を含浸し、溶媒を除去して複合高分子固体電解質膜を形成し、引き続いてその表面に第２の延伸多孔質ＰＴＦＥ膜を配置し、その表面に少なくとも電極触媒と高分子固体電解質とを含むインク状溶液を塗布することにより、第２の延伸多孔質ＰＴＦＥの空隙中にインク状溶液を含浸した後、溶媒を除去することにより電極を複合高分子固体電解質膜表面に形成して得ることができる。

【００３１】ここで、予め成形された電極としては、Ｐ

Ｅ膜を使用する電気化学装置に使用される電極であれば、全て適用可能であるが、複合ＰＥ膜との接着性を増すために、予めＰＥ溶液を塗布しておく必要のある場合もある。この様な電極としては、各種触媒粉末をＰＴＦＥ等の樹脂で結着したもの、あるいはこの表面にＰＥ樹脂を塗布含浸したもの等が挙げられるが、より好ましくは、離型性を有する基材、あるいは導電性で且つ撥水性を有するいわゆるガス拡散層材料面上に、前述のインク状溶液を塗布、乾燥して得た電極が好ましく、特には、離型性を有する基材またはガス拡散層材料面上に前述したのと同様にしてＥＰＴＦＥの空隙中に少なくとも電極触媒とＰＥ樹脂を含む電極構成成分が充填されて成る電極が好ましい。もちろん離型性を有する基材上に電極を構成した後、本発明の電極／膜／電極の接合体を構成した場合には、これを構成した後、この基材を最後に取り除くのは前述したのと同様であるが、ガス拡散層材料面上に構成した場合には、そのまま使用することになる。

【００３２】以上の説明でわかる通り、本発明によれば電解質膜／電極の接合体または電極／電解質膜／電極の接合体を得ることができるが、本発明ではさらに集（給）電体との接合も同時に行ってもよい。この集（給）電体と一体に成形する場合、上記の含浸を行った後、まだ溶媒を除去しないうちに後述するような集（給）電体またはガス拡散層材料面上に固定した後、溶媒を風乾等により除去することにより、溶媒及び高分子固体電解質樹脂の凝集力により、高分子固体電解質樹脂をバインダーとして、接合、一体化する。別の一体化成形方法としては、集（給）電体またはガス拡散層材料面上にＥＰＴＦＥフィルムを固定した後、前述の混合溶液を塗布するか、またはさらにこれをロール等に通すことによりＥＰＴＦＥの空隙中に溶液を含浸した後風乾等により溶媒を除去し、接合、一体化することもできる。

【００３３】以上の何れの方法においても、高分子固体電解質樹脂の種類によって、最終的に加熱等の手段により、樹脂を安定化する必要のある場合もある。図１（Ａ）（Ｂ）に本発明の（電極／）複合高分子固体電解質膜／電極一体形成体を示す。図１中、１は複合高分子固体電解質膜、２は電極、３は高分子固体電解質膜のＥＰＴＦＥの微小結節、４はＥＰＴＦＥの微細繊維、５は高分子固体電解質、６は少なくとも電極触媒と高分子固体電解質を含む電極構成成分である。

【００３４】一般に、本発明の電解質膜／電極の接合体の用途では、多くの場合集電体または給電体とともに用いられ、特に燃料電池の場合、さらに、その間に導電性の撥水性ガス拡散層が設けられることも多い。集（給）電体としては、ニッケル、チタン、銅、ステンレス等のメッシュまたはエクスパンドメッシュ、あるいはこれらメタルメッシュに金や白金族のメッキまたはコーティングしたもの、ポーラスカーボンまたはグラファイト、カーボンペーパー等が使用される。

【００３５】また、撥水性ガス拡散層としては上記集（給）電体の材料と同様のものをＰＴＦＥで撥水処理したものや、ＰＴＦＥとカーボンブラックまたは黒鉛等の導電性粉末を混ぜ合わせて上記集（給）電体にプレス等により一体に成形したもの、ペースト状にして塗布し、乾燥焼成して成形したもの、混練してシート状に成形したもの、さらにこれを延伸してより多孔度を上げたもの等がある。

【００３６】以上の如き本発明の電解質膜／電極接合体を各種の電気化学装置に使用する仕方は、本発明の電解質膜／電極を用いる以外従来と同様であることができる。図２に燃料電池の例を示す。図２中、１は高分子固体電解質、２は電極、７，８は集（給）電体、９，１０はセパレータ板、１１，１２はガス供給溝、１３はガス拡散層シートである。必要に応じて本発明の高分子固体電解質１／電極２の接合体又は電極２／高分子固体電解質１／電極２の接合体は集（給）電体との接合体として使用することができる。

【００３７】こうして構成された高分子固体電解質燃料電池では、図２を参照すると、ガス供給溝２８にO_2を溝２９にH_2を供給すると、電極２２内で$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$、電極２３内で$2H_2 \rightarrow 4H^+ + 4e^-$の反応が起こり、$4H^+$は高分子固体電解質２１を通って電極２３から電極２２へ流れ、$4e^-$は外部負荷を通ることにより電気エネルギーとなる。作動温度は６０℃から１００℃程度、好ましくは８０℃程度である。

【００３８】なお、本発明の電解質膜／電極は高分子固体電解質燃料電池のほか、水電解装置やオゾン発生器などにも使用できる。

【００３９】

【実施例】

実施例１

ＰＰシートの表面に膜厚１０μｍ、空隙率８３％、最大孔径がＥＢＰ値で１．７５Kg／cm²のＥＰＴＦＥフィルムを固定した後、その表面に濃度５wt％のパーフルオロスルフォン酸樹脂溶液を塗布することによりＥＰＴＦＥフィルムの空隙部に含浸したのち７０℃で風乾することにより溶媒を除去して樹脂をフィルム中に固定した。この操作を４回繰り返すことによりＥＰＴＦＥフィルムの空隙部に樹脂を十分に含浸固定して、ほぼ透明な複合高分子固体電解質膜を得た。このとき、この複合高分子固体電解質膜は、ＰＰシートに十分固着しており、ほぼ一体のシートとして取り扱える状態であった。

【００４０】これとは別に、白金を３０wt％担持したカーボンブラック（以後ＰｔＣと略す）３にたいしてパーフルオロスルフォン酸樹脂１の割合で混合した濃度１０wt％インク状溶液を用意した。次に、先に用意したＰＰシート／複合高分子固体電解質膜の複合高分子固体電解質膜表面に、膜厚１０μｍ、空隙率９１％、最大孔径がＥＢＰ値で０．１３Kg／cm²のＥＰＴＦＥフィルムを固

定した後、前記インク状溶液をその表面に塗布することにより、このＥＰＴＦＥフィルムの空隙部にインク状溶液を含浸し、７０℃で風乾することにより溶媒を除去して、複合高分子固体電解質表面にＥＰＴＦＥフィルム空隙部および内部構造表面にＰｔＣと高分子固体電解質樹脂がまつわりついた形の触媒層を一体に形成した。その後、ＰＰシートからこの一体成形体を剥しとって、本発明の複合高分子固体電解質膜／電極一体成形体を得た。

【００４１】実施例２

実施例１で得た一体成形体を２枚、複合高分子固体電解質面をつき合わせて重ねた後、１５０℃に加熱した一対のロール間に通すことにより熱酸着させて一方の面を空気極、もう一方の面を水素極として、図２の様にカーボンブラックとＰＴＦＥとからなるガス拡散層シートではさみ、更にその外側にＰＴＦＥで撥水処理したカーボンペーパーを配置した後、リブ付きセパレータ板で押さえ込むことにより、燃料電池を構成した。そして、この燃料電池を発電させたところ、０．５Ａ／cm² の電流密度で０．６４Ｖの出力が得られた。またこの時の交流抵抗値は約０．０７オーム・cm² であり、これらの値は８００時間運転後もほとんど変化しなかった。

【００４２】実施例３

実施例１においてＰＰシートの上に固定したＥＰＴＦＥフィルムとして膜厚６μｍのものを使用し、また高分子固体電解質樹脂の塗布含浸を２回とした他は同様にして本発明の複合高分子固体電解質膜／電極一体成形体を得た。次に別に用意した膜厚５０μｍの溶融成形によるパーフルオロスルフォン酸膜を間にして本発明の一体成形体を２枚複合高分子固体電解質膜面が向き合うように配置して、１４０度Ｃ、３０kg／cm² の圧力でホットプレスすることにより一体に接合した。この接合体を用いて実施例２と同様にして燃料電池を構成し、酸素水素を供給して発電させたところ、１Ａ／cm2 の電流密度で約０．６Ｖの出力が得られた。

【００４３】実施例４

膜厚７０μｍのＰＰシートの上に、実施例１で使用したのと同じ膜厚１０μｍ空隙率９１％のＥＰＴＦＥフィルムを配置し、実施例１で使用したのと同じインク状溶液をその表面に塗布することにより、ＥＰＴＦＥフィルム中で含浸し、溶媒を除去して、ＥＰＴＦＥフィルム空隙中にＰｔＣと高分子固体電解質樹脂との混合物が含有された電極を形成した。この電極はＰＰシートに良く固着していた。

【００４４】続いて更にこの表面に、膜厚１８μｍ空隙率８５％のＥＰＴＦＥフィルムを配置した後、その表面に濃度９wt％のパーフルオロスルフォン酸樹脂溶液を塗布し、引き続いて７０℃で風乾した。この工程を５回繰り返すことにより、このＥＰＴＦＥフィルム空隙中にパーフルオロスルフォン酸樹脂を含浸固定して、電極表面上に一体に複合高分子固体電解質膜を形成させた。

【００４５】次に、更にこの表面に先に使用したのと同じ膜厚１０μｍ、空隙率９１％のＥＰＴＦＥフィルムを配置し、やはり同じインク状溶液を塗布、含浸、溶媒除去することにより、このＥＰＴＦＥフィルム空隙中にＰｔＣと高分子固体電解質樹脂との混合物が含有された電極を複合高分子固体電解質膜上に一体に形成して、ＰＰシート上に電極／複合高分子固体電解質膜／電極一体成形体を形成した後、ＰＰシートから剥しとって本発明一体成形体を得た。

【００４６】実施例５

実施例４で得られた一体成形体を実施例２と同様にして、水素－空気燃料電池を構成し発電させたところ、０．５Ａ／cm² の電流密度で０．６２Ｖの出力が得られた、またこのときの交流抵抗値は０．０６５オーム・cm² であった。

【図面の簡単な説明】

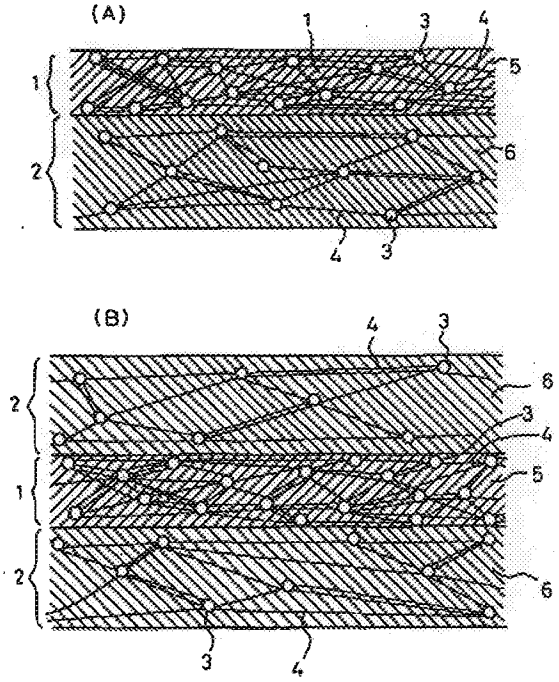
【図１】本発明の複合高分子固体電解質膜／電極一体形成体（Ａ）及び電極／複合高分子固体電解質膜／電極一体形成体（Ｂ）の断面図である。

【図２】燃料電池の例を示す断面図である。

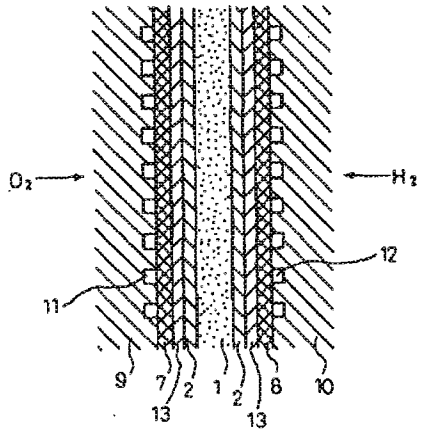
【符号の説明】

１…複合高分子固体電解質膜
２…電極
３…微小結節
４…微細繊維
５…高分子固体電解質樹脂
６…電極触媒・高分子固体電解質樹脂混合物
７，８…集（給）電体
９，１０…セパレータ板
１１，１２…ガス供給溝

【図１】



【図２】



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